Synthesis and properties of soluble phthalazinone-based polybenzimidazoles for proton exchange membranes

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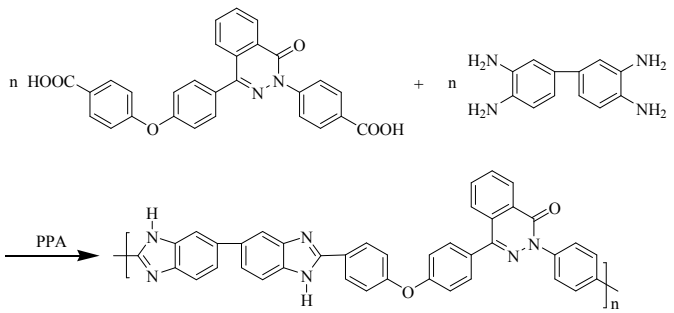
Polybenzimidazole (PBI), also known as Celazole® or poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole), is one of the classes of aromatic heterocyclic polymers, which has high mechanical properties, excellent thermal stability and chemical resistance. Because of these outstanding comprehensive properties, they have been widely used in automotive industry[1], aeronautical industry[2], microelectronics industry[3, 4], fuel cells components[5], etc. However, the major drawback of PBIs is their extreme processing conditions due to the poor solubility and infusibility for the rigid polymer backbones and the strong intermolecular hydrogen bonding. Lots of efforts have been afforded to improve the solubility of PBIs by structural modification[6,7]. Phthalazinone moiety is a heterocyclic, crank and twisted, non-coplanar and asymmetrical structure, which can reduce the regularity of the main chain, cumber the close packing of chains and increase the free space between the molecular chains, and thus enhance the solubility of polymers. In this study, novel series of polybenzimidazoles containing phthalazinone moiety in the polymer main chain have been synthesized. Their applications in proton exchange membrane fuel cells have been studied. The relationship between polymer structure and membrane properties has been discussed.

1. Synthesis of polybenzimidazoles containing phthalazinone moiety



Scheme 1. Synthesis of homo- polybenzimidazoles containing phthalazinone moiety

A novel polybenzimidazole containing phthalazinone structure (PPBI) [8] was synthesized from 4-(4-(4-(4-Carboxyphenoxy)phenyl)-1-oxophthalazin-2(1H)-yl)benzoic acid (**CPPBC**) and 3,3'-diaminobenzidine (DAB) by solution polycondensation in polyphosphoric acid (PPA), as shown in Scheme 1. The PPBI polymer was found to be soluble in aprotic polar solvents such as H_2SO_4, N-methyl-2-pyrolidinone (NMP), N, N-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO),

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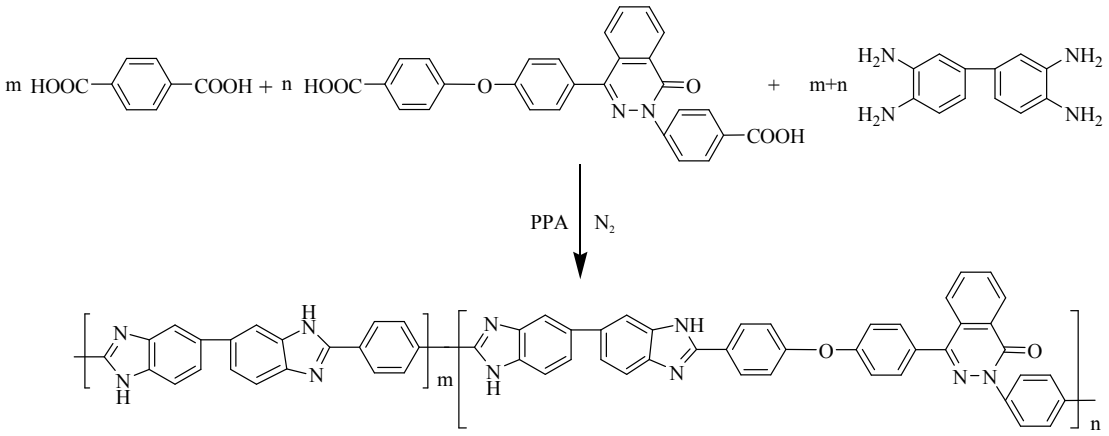
without the addition of inorganic salts. The PPBI has inherent viscosity of 1.78 dL/g, and showed amorphous nature as evaluated by WAXD. PPBI has high glass transition temperatures (T_g) of 402 °C and excellent thermal stability with the temperatures for 5% and 10% polymer weight loss of 535 °C and 572 °C, respectively. The char yields (C_y) of PPBI at 800 °C was 66.0% in N_2.



Scheme 2 Synthesis of p-PPBIs

A novel series of polybenzimidazoles containing phthalazinone moieties and p-phenylene linkages (p-PPBI) were synthesized from CPPBC, terephthalic acid (TPA) and DAB in PPA, as shown in Scheme 2. The chemical structures of p-PPBI polymers were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and WAXD. The resultant polymers have inherent viscosities from 1.99 to 3.43 dL/g in 96% sulfuric acid at 30 °C and show good solubility in aprotic polar solvents, such as NMP, DMAc and DMSO. These *p*-PPBI polymers exhibit high glass transition temperatures (Tg) in the range of 399-426 °C and excellent thermal stability with the 5% ($T_{d5\%}$) and 10% ($T_{d10\%}$) weight loss temperatures in the range of 501 to 564 °C and 590 to 640 °C, respectively. The char yields (Cy) of *p*-PPBI at 800 °C were in the range of 74.2-80.9%.

Table 1 Inherent viscosity and solubility of *p*-PBI, PPBI, and *p*-PPBIs

Polymer	I.V. (dL/g)	H2SO4 (96%)	NMP	DMAc	DMSO	DMF	H_3PO_4(85%)	THF	CH_3Cl
p-PBI[28]	3.22	++	-	-	-	-	-	-	-
p-PPBI-20	2.86	++	++	++	++	+-	-	-	-
p-PPBI-40	3.43	++	++	++	+-	+-	-	-	-
p-PPBI-60	2.94	++	++	++	++	+-	-	-	-
p-PPBI-80	3.24	++	++	++	+-	+-	-	-	-
PPBI	1.78	++	++	++	++	+-	-	-	-

++：solubility in room temperature；+-：partially soluble；-：insoluble;

NMP：*N*-methyl pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethyformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

2. Preparation and properties of PEM membranes derived from PPBIs

The amorphous PPBI and *p*-PPBI polymers were cast into membranes by solution casting method, doped with phosphoric acid and further investigated as proton exchange membranes [9]. To modify the doping conditions, the PPBI membranes were doped in PA with different concentration, at different

doping temperature and for different time. Membranes with high acid doping level (～15.2 mol H_3PO_4) and high proton conductivity (～0.13 S/cm in anhydrous condition) were obtained after doping with 85 wt% phosphoric acid at 180 °C for 30 h. These obtained membranes present good oxidative stability and mechanical property even with high doping levels.

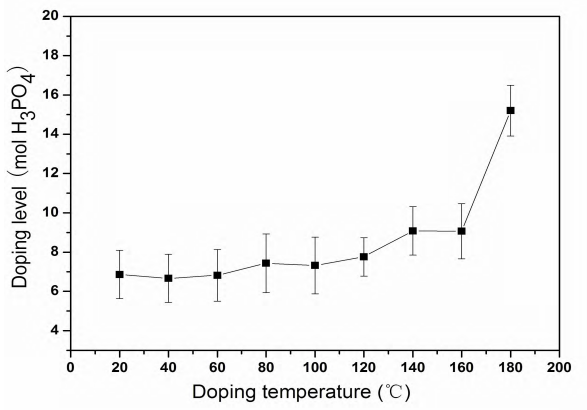


Figure 1. Doping level of the membranes doping in phosphoric acid at different temperature

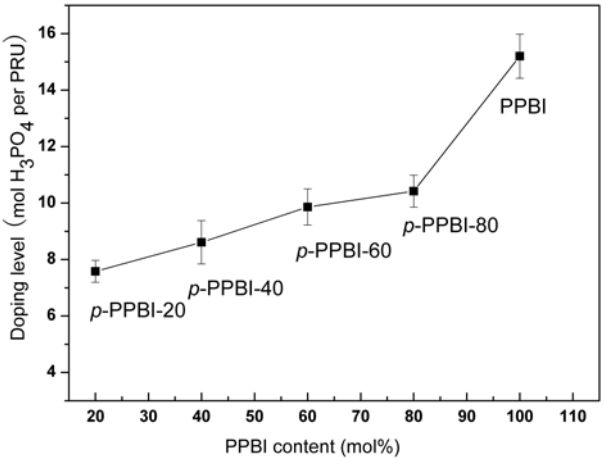


Figure 2 Doping levels of *p*-PPBIs

As shown in Figure 1, the doping level increased as the increasing of the doping temperature. Moreover, the doping level increases with the increasing content of phthalazinone moiety (Figure 2), which indicates the introduction of phthalazinone moiety could enhance the acid absorbing ability of PBI. The twisted non-coplanar phthalazinone structure could destroy the crystalline structure and reduce the intra- and intermolecular forces. The loosing polymer chain packing of PBI containing phthalazinone moieties and p-phenylene linkages is beneficial for the absorption of phosphoric acid.

The conductivity of the membranes varies with the doping level and testing temperature. Membranes of higher doping level obtained higher conductivity. Meanwhile, the conductivity increase slightly with the increasing of testing temperature, as shown in Figure 3. The nitrogen atoms and carbonyl groups in phthalazinone structure should facilitate proton transfer because of comparatively weak hydrogen bonding, which helps to exchange protons due to less friction.

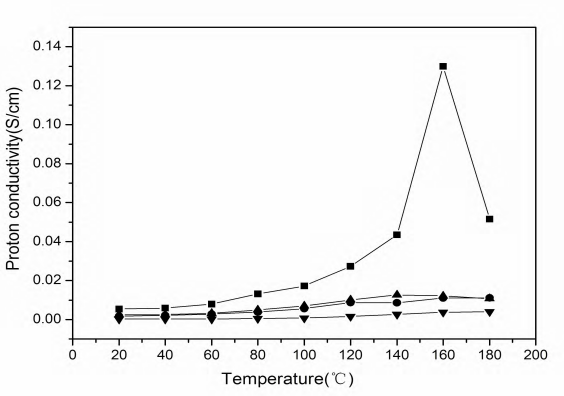
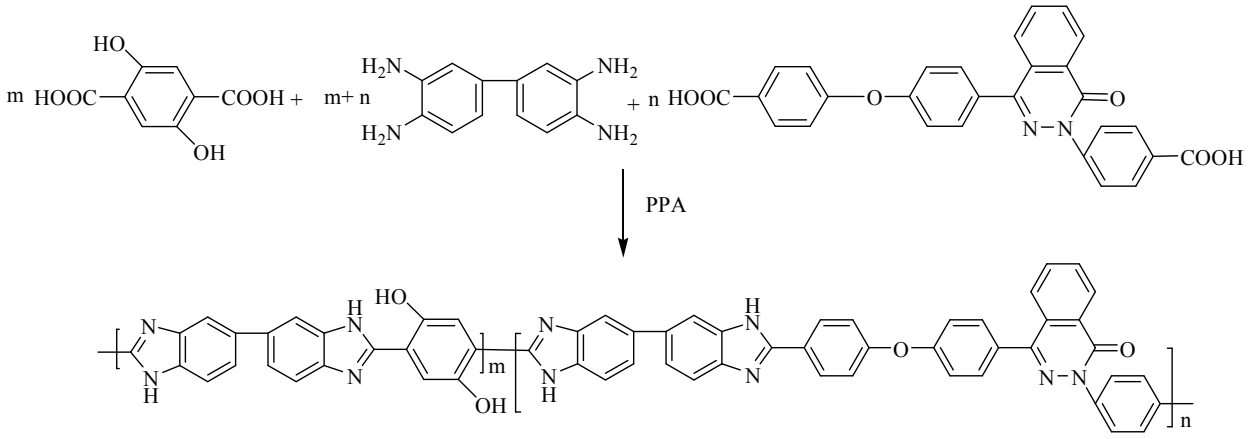


Figure 3. The proton conductivity of the membrane with different doping level
■ membrane with doping level of 15.2 ●membrane with doping level of 7.97
▲membrane with doping level of 4.84 ▼membrane with doping level of 2.98

3. Functional PPBI containing hydroxyl groups

A series of novel polybenzimidazoles containing phthalazinone moieties and functional hydroxyl groups (PPBIOH)[10] were synthesized from CPPBC, 2,5-dyhydroxyterephthalic acid (TPA-OH) and DAB in PPA. The resultant polymers showed good solubility in 98% H_2SO_4 and NMP. The inherent viscosities of the polymers in 98% H_2SO_4 at 25 ^oC were in the range of 0.33-2.10 dL/g, increasing obviously with decreasing hydroxyl content in the main chain. The corresponding acid doped membranes were prepared directly from the polymerization solution by the PPA process. These membranes showed reasonable doping levels (10.1-12.2 mol H_3PO_4), high proton conductivities (0.10-0.21 $S \cdot cm^{-1}$ above 120 ^oC), and high oxidative stability (breaking time in the range of 52-155 h). The structures of PPBIOH membranes were analyzed by theWAXD, and exhibited semi-crystalline character, from which the mechanism of proton conduction can be further investigated. The combination performance makes these PPBIOH membranes promising candidates for potential applications in high-temperature proton exchange membrane fuel cells (PEMFCs).



Scheme 3 Synthesis of PPBIOHs

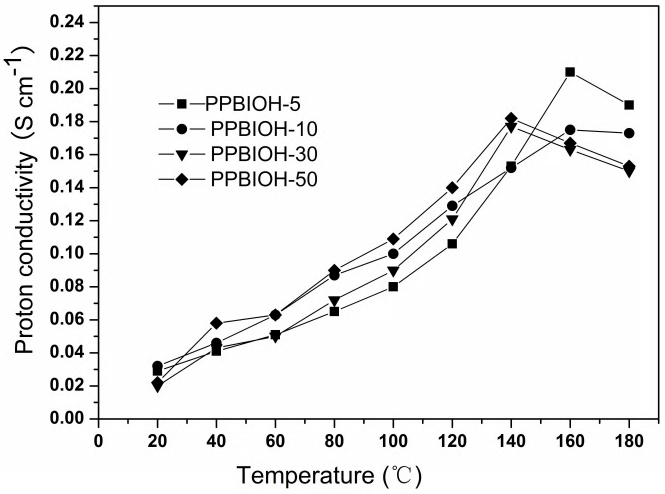
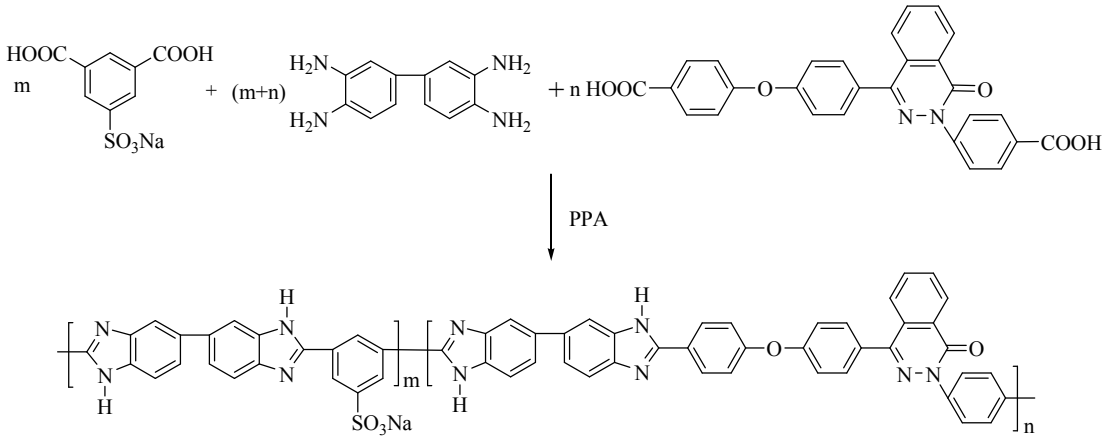


Figure 4 Proton conductivity curves of the PPBIOH membranes with increasing temperature

Table 2 Doping level and mechanical properties of PPBIOH membranes

Membrane	Doping level (mol H_3PO_4)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PPBIOH-5	12.2	29.3	2.9	28.1
PPBIOH-10	11.3	27.8	2.5	48.6
PPBIOH-30	10.1	21.7	2.5	55.9
PPBIOH-50	10.6	9.1	1.7	68.0

4. Sulfonated polybenzimidazoles containing phthalazinone moiety



Scheme 4 Synthesis of sulfonated polybenzimidazoles containing phthalazinone moiety

A novel series of sulfonated phthalazinone-based polybenzimidazoles (SPPBI) [11] are synthesized by solution polycondensation of DAB, CPPBC and 5-sulfoisophthalic acid monosodium salt (SIPN) in PPA. Their chemical structures are characterized by NMR, FTIR and WAXD, and the inherent viscosities in DMAc are from 1.49 to 1.78 dL/g. The SPPBIs exhibit good solubility in polar aprotic organic solvents, such as NMP, DMAc and DMSO. The SPPBI membranes are prepared by solution casting technique using DMSO as solvent. The SPPBIs show excellent thermal stability, and their

membranes display low water uptake, low swelling ratio, good mechanical properties and excellent resistance to oxidation. The SPPBI membranes have unexpected low methanol permeability (5.46×10^{-10}-1.27×10^{-9} cm^2/s), and their proton conductivities are comparable with Nafion® 117 at the temperature below 100 °C (~1.3×10^{-2} S/cm at 80 °C in water).

Table 3 Methanol permeabilities, IEC, water uptake, swelling ratio and proton conductivities of sPPBI membranes and Nafion® 117

Membrane	*Methanol permeability(cm^2/s)*	*IEC (meq/g)*		*Water uptake (%)*		*Swelling ratio (%)*		Proton conductivity[a] (S/cm)	
		Cal.	Meas.	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C
sPPBI-20	5.46×10^{-10}	0.35	0.22	5.1	13.0	1.9	3.8	2.3×10^{-3}	4.8×10^{-3}
sPPBI-30	7.86×10^{-10}	0.55	0.43	5.8	13.6	3.0	4.3	3.8×10^{-3}	5.4×10^{-3}
sPPBI-40	9.85×10^{-10}	0.76	0.62	9.3	14.5	3.1	5.8	4.6×10^{-3}	7.8×10^{-3}
sPPBI-50	1.27×10^{-9}	0.99	0.76	10.0	15.7	5.0	7.3	8.5×10^{-3}	1.3×10^{-2}
Nafion® 117	2.4×10^{-6}	0.90		19.6	30.0	15.0	21.5	7.5×10^{-2}	9.6×10^{-2}

[a] Measured in water (RH100%)

Acknowledgements

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